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New PVDF microcapsules for application in catalysis

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Abstract

Novel polyvinylidene fluoride (PVDF) porous microcapsule membranes were successfully prepared with non-solvent induced phase inversion method for the immobilization of catalyst ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$).

The chemical–physical analysis of the new PVDF catalytic microcapsules was carried out by means of SEM, EDX, IR, DSC and XRD techniques.

Catalytic activity of the PVDF catalytic microcapsules has been evaluated in the oxidation of benzyl alcohol to benzaldehyde in solvent free conditions. The polymeric microcapsules ''keep in contact'' the two phases: the organic phase, containing the substrate and the product, and the aqueous phase with the oxidant, H_2O_2. In literature, ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) was reported to be effective in the oxidation of alcohols with H_2O_2 in combination with a phase transfer catalyst in chlorinated solvents.

The effect of reaction temperature, substrate:oxidant ratio, swelling of polymeric microcapsules on the reaction progress was investigated.

PVDF catalytic microcapsules have given proof of their complete stability under oxidation conditions and their good recycle.

Keywords: Catalytic polymeric microcapsules; Selective oxidation; Polyvinylidene fluoride; Ammonium molybdate tetrahydrate; Phase inversion

1. Introduction

Catalytic oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones are essential reactions in organic synthesis [1,2]. Conventional methods for performing such transformations generally involve the use of stoichiometric or more than stoichiometric quantities of inorganic oxidants, such as chromium(VI) reagents, dimethyl sulfoxide, permanganates, periodates, or *N*-chlorosuccinimide (NCS) [3]. Even though these homogeneous catalyses show good catalytic performance, problems related to corrosion and plating out on the reactor wall, handling, recovery, and reuse of the catalyst set up limitations of their use in industrial scale [4]. Besides, safety hazards associated with these oxidants and their toxic by-products and waste are also the major problems of such processes. Furthermore, these methods are usually carried out in halogenated organic solvents, typically chlorinated hydrocarbons which are environmentally undesirable and often require one or more equivalents of these relatively expensive oxidizing agents. From both economic and environmental point of view, there is a growing demand for new, environmentally benign and economic heterogeneous catalytic methods. Many heterogeneous catalysts have since been developed, but most of them were based on noble and rare metals, cost expensive and some of them required inert atmosphere during the preparation of the catalyst. Sometimes they even need other promoter ions to achieve good catalytic activities [5,6].

In our early paper [7], we reported a novel method for selective oxidation of benzyl alcohol to benzaldehyde. A polymeric microporous membrane acts as a barrier to ''keep in contact'' the organic phase containing benzyl alcohol and the aqueous phase with hydrogen peroxide. The membrane's role in this system was to improve the contact between the two different reactive phases, the catalyst being physically separated from the membrane, realizing an inert membrane reactor [8–10].

In this study, we report on the preparation, characterization and use of new heterogeneous catalyst for the selective

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oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH). The catalyst, ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, was entrapped inside PVDF polymeric microcapsules during their preparation by means of phase inversion technique induced by non-solvent [11]. Every microcapsule works as a catalytic membrane reactor with both the catalytic and contactor functions [10]. Common techniques for fabricating hollow microcapsules with dense or porous membranes include interfacial polymerization, in situ polymerization [12–25], and phase inversion [26–30]. In particular, using phase inversion method, microcapsule membranes based on cellulose acetate (CA), ethylcellulose (EC) [26,27], polyethersulphone (PES) [28,29] and a modified polyetheretherketone (PEEKWC) [30] characterized by pore microstructure both straight and packed throughout the whole membrane thickness were prepared. These morphological properties were obtained by using additives in the polymeric solutions as LiCl, PVP and PEG400 [28,30] or acetone, alcohol, glycerin, or TEC in various ratio [26], that are responsible for an increase of demixing rate and for a more porous structure [11].

The new PVDF catalytic microcapsules, reported in this work, were prepared by means of phase inversion induced by non-solvent without use of additives in the polymeric solutions to prevent catalyst deactivation: the demixing rate between the polymer solvent (*N*,*N*-dimethylformamide) and the coagulant (a mixture 1:1 of isopropapnol and water) affected the final open structure of microcapsule core.

PVDF microcapsules, featured with a reservoir-type porous microcapsule membrane structure and with numerous straight microchannels across the membrane have been obtained. The hollow structure could provide large space for immobilizing the catalyst inside the proposed microcapsule, and the straight microchannel structure across the membrane could significantly reduce the mass transfer resistance.

Microcapsules have found numerous applications in various fields, such as pharmaceutical, chemical, textile, biomedical, environmental, petroleum and pesticide industries, and so on [31–33].

In particular, in the field of catalysis, when encapsulating a catalyst or enzyme, a potentially high interfacial specific area is created and the recovery of the catalyst is facilitated. The selective sorption through the membrane can further increase catalytic performances. Okahata and Ariga [34] introduced the concept of capsule membrane supported phase transfer catalysts (CM-PTC). The phase transfer catalyst (PTC) is used to transfer a reactant form one phase to another so that reaction occurs. In CM-PTC the PCs were grafted onto the surface of an ultrathin, porous capsule membrane based on nylon. The capsules were prepared via interfacial polycondensation.

Yadav and Mehta [35] also used nylon capsules. They were prepared by adding dropwise a basic solution of amine to an organic solution of terephtahloyl chloride that also contained the trimesoyl chloride cross-linker. The tetra-alkylammonium PTCs were supported on the thus obtained thin (7.6 μm), small (1.7 mm) nylon capsule and were subsequently filled with benzyl chloride. The filled capsules were then added to an aqueous solution of hydrogen peroxide. The H_2O_2 was transfer to the organic phase as a solvate of the PTC, which simultaneously prevented its decomposition.

The group of Vorlop developed an interesting type of entrapment of (bio)catalysts in polymers such as PDMS, PVA [35] introducing a new route to prepare micro-encapsulated liquid membranes: carrier molecules that can be reversibly bind oxygen molecules are first encapsulated together with a suitable solvent and the capsules dispersed in a polymer matrix to obtain a homogeneous carrier-containing liquid membrane. These systems were mainly used for nitrate and nitrite reduction and in the synthesis of fine chemicals [36].

In the oxidation of BzOH to BzH using, for the first time, PVDF catalytic microcapsules, described in this work, the effect of reaction temperature, substrate:oxidant ratio, swelling of polymeric microcapsules on the reaction progress was investigated.

From both an economic and environmental viewpoints, the new catalytic microcapsules, working with an environmentally suitable oxidant, H_2O_2 and in absence of organic solvents, recyclable without loss of activity and selectivity, represent an answer for a more-sustainable industrial growth.

2. Experimental section

2.1. Chemicals

For the preparation of catalytic microcapsules, PVDF (Solef 6010) was supplied by Solvay, and was used without purification. *N*,*N*-dimethylformamide (DMF) was purchased from Fluka. Water, used for the coagulation bath, was double distilled. Isopropanol from Carlo Erba was added in the coagulation bath as non-solvent.

Acetonitrile was purchased from Sigma–Aldrich.

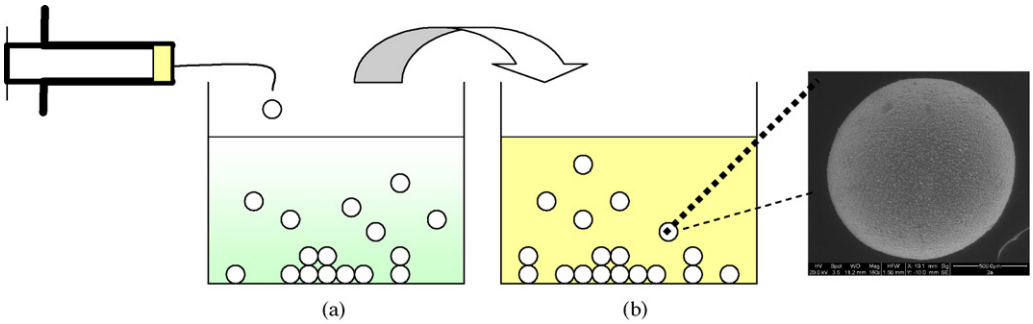
Ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (MW = 1235.86 g/mol, purity 99.98%), from Sigma–Aldrich was employed as catalyst.

For the reaction studied, BzOH (MW = 108.14 g/mol, purity 99.99%) from Sigma–Aldrich was used both as reagent and as solvent. BzH (MW = 106.12 g/mol, purity 99.99%) and BzA (MW = 122.12 g/mol, purity 99.99%) from Sigma–Aldrich were used for analytical calibrations. Hydrogen peroxide H_2O_2 (30 wt% solution in water) from Sigma–Aldrich was the oxidant.

2.2. Preparation of catalytic microcapsules

The preparation procedure is illustrated in Scheme 1.

The fabrication process route of the proposed microcapsules was simple and effective. Microcapsules with a dense skin layer were prepared by means of phase inversion technique induced by non-solvent. A mixture of polymer PVDF (5 g), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1 g), was dissolved in 44 g of DMF solvent by stirring. To eliminate the air bubbles in the solution, the polymer solution was placed still for 2 h at room temperature before using. The polymer solution was gradually dropped dropwise into a mixture water/isopropanol 1:1 (v/v) coagulation bath through a syringe needle using a syringe



Scheme 1. Schematic illustration of the PVDF microcapsule membrane preparation: (a) precipitation of microcapsules in isopropanol:water 50% (v/v) mixture due to phase inversion phenomenon induced by solvent–non-solvent diffusion; (b) washing of the residual solvent (DMF) in pure isopropanol bath.

pump. The temperature of the coagulation solution was kept at a constant 30 °C using a thermostatic unit. The microcapsules were immersed and washed in the isopropanol bath for 24 h, then dried in a vacuum oven at 50 °C overnight.

2.3. Characterization

The formed membranes were characterized by the following methods:

(1) The morphology of the catalytic capsules was evaluated by means of SEM at 20 kV (Cambridge Instruments Stereoscan 360).
(2) The diameter of the microcapsules was determined by a digital micrometer (Carl Mahr D 7300 Esslingen A.N.) and by SEM observation of the freeze-fractured cross-sections.
(3) The success of entrapment of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and its uniform dispersion in the polymeric microcapsules was evaluated by energy dispersive X-ray (EDX) (Philips EDAX analysis system) and back scattering electron (BSE) (Cambridge Instruments Stereoscan 360) techniques.
(4) FT-IR spectra of the prepared films were recorded with a PerkinElmer Spectrum One over a range of 4000–400 cm^{-1}.
(5) Thermal properties of the PVDF microcapsules, catalytic PVDF microcapsule and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were evaluated by DSC analysis. Measurements were carried out on a Pyris Diamond Differential Scanning Calorimeter (PerkinElmer). Samples of about 8 and 15 mg were subjected to a heating/cooling/heating cycle at a rate of 15 °C/min in the range of 50 and 220 °C. An empty pan with two covers was used as the reference.
(6) X-ray diffractograms were collected by a Philips PW 1710 powder diffractometer, using Cu Kα radiation, with the generator working at 40 kV and 55 mA. Intensities were measured in the range $5 < 2\Theta < 35$, typically with 0.8 s/step.
(7) Swelling experiments have been carried out using samples dried at 60 °C for 24 h.

The microcapsules were immersed at 25 °C in solutions of the substrate BzOH and acetonitrile. Membrane swelling was monitored until the microcapsules had reached a constant weight. Samples were withdrawn from the solvent and weighed after removal of the surface solvent by light blotting with a filter paper.

2.4. Oxidation reaction

The performance of the PVDF catalytic microcapsules was investigated under batch conditions using comparable total catalyst loading.

A typical procedure for oxidation of BzOH is below reported. An amount of microcapsules containing 0.185 mmol of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ was kept at 40 °C for 24 h in pure BzOH.

Then, PVDF catalytic microcapsules were immersed in a 25 ml volumetric flask with 9.26 mmol of BzOH and 9.20 mmol of H_2O_2 (unless otherwise stated). Reaction temperature was maintained constant by immersing the reactor in a constant temperature oil bath.

The microcapsules were washed three times before a catalytic run using acetonitrile in which both substrates and products are perfectly soluble. At the end of each run, for the substrate the balance mass showed that the membranes did not retain it; for the product, the weight of the washed microcapsules before and after catalytic test was unvaried.

Obtained results are reported as selectivity to BzH, BzOH conversion to BzH, H_2O_2 conversion to BzH at a reaction time of 4 h.

The analysis of the organic phase was carried by GLC using a 6890 network GC system of Agilent on a HP-5 (30 m × 0.320 mm × 0.25 μm) column.

3. Results and discussion

3.1. Microcapsule characterization

The microcapsules showed a satisfactorily spherical appearance as shown by SEM analysis of Fig. 1, and the diameter was about 1.3 mm, which could be adjusted by changing the syringe needle and the blowing gas flow outside the needle. Using back scattered electron (BSE) analysis (Fig. 1, right), the catalytic particles can be visualized as white spots in the dark membrane

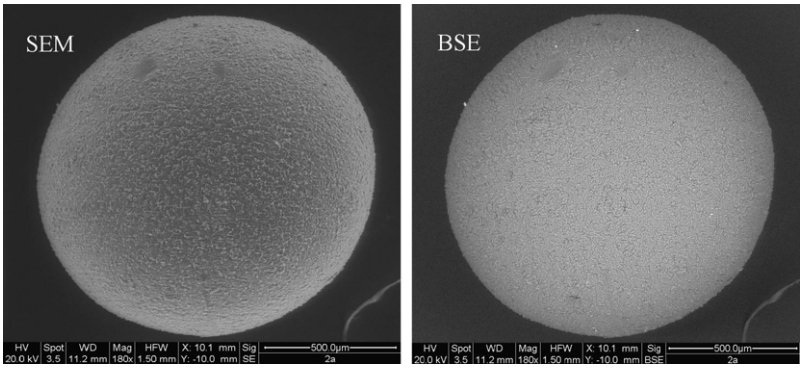


Fig. 1. SEM and BSE images of the catalytic PVDF microcapsule membranes: external surface of the whole microcapsule.

matrix. An uniform catalyst distribution on the microcapsules surface also at high magnification (Fig. 2c, top) was obtained.

Noteworthy, the morphology of the PVDF microcapsules without catalyst was different from that observed for PVDF catalytic microcapsules: shell surface do not show pores (Fig. 2a, top) and the inner of microcapsule is dense without channels and macrovoids (Fig. 2a, bottom).

A hollow structure with a porous rough inner surface, was clearly visible for the PVDF catalytic microcapsule (Fig. 2b, bottom). It was reasoned that the ideal membrane of the microcapsule entrapping the catalyst should be externally skinned with a spherical wall consisting entirely of narrow bore, closely packed, finger-like cavities, radiating inwards from just below the skin layer.

The identification of the white spots (uniformly dispersed) as catalyst was carried out by EDX analyses. In Fig. 3, EDX analyses of two slices 30 μm × 30 μm on different point of microcapsule surface have been reported. In the two analyses, the intensity of Mo signal respect with signal of F of the polymeric matrix was the same, confirming the homogeneous catalyst distribution observed on the basis of visual BSE analysis.

In Fig. 4 the distributions of the PVDF microcapsule diameters with and without catalyst have been reported.

For the PVDF catalytic microcapsules, the diameter size distribution was from 1 to 1.6 mm with a max on 1.2 mm. However, PVDF microcapsules without catalyst showed a max on 1.0 mm.

The increased microcapsule diameter (from 1.0 to 1.2 mm, respectively) and the different morphology observed (as reported in Fig. 2) for neat and catalytic PVDF microcapsules can be explained on the basis of the phase inversion process occurring during the microcapsule formation. The presence of catalytic salt increased the demixing rate and gelation of the polymer rich phase, which allows a stronger extension of the polymeric film in a perpendicular direction. The effect of

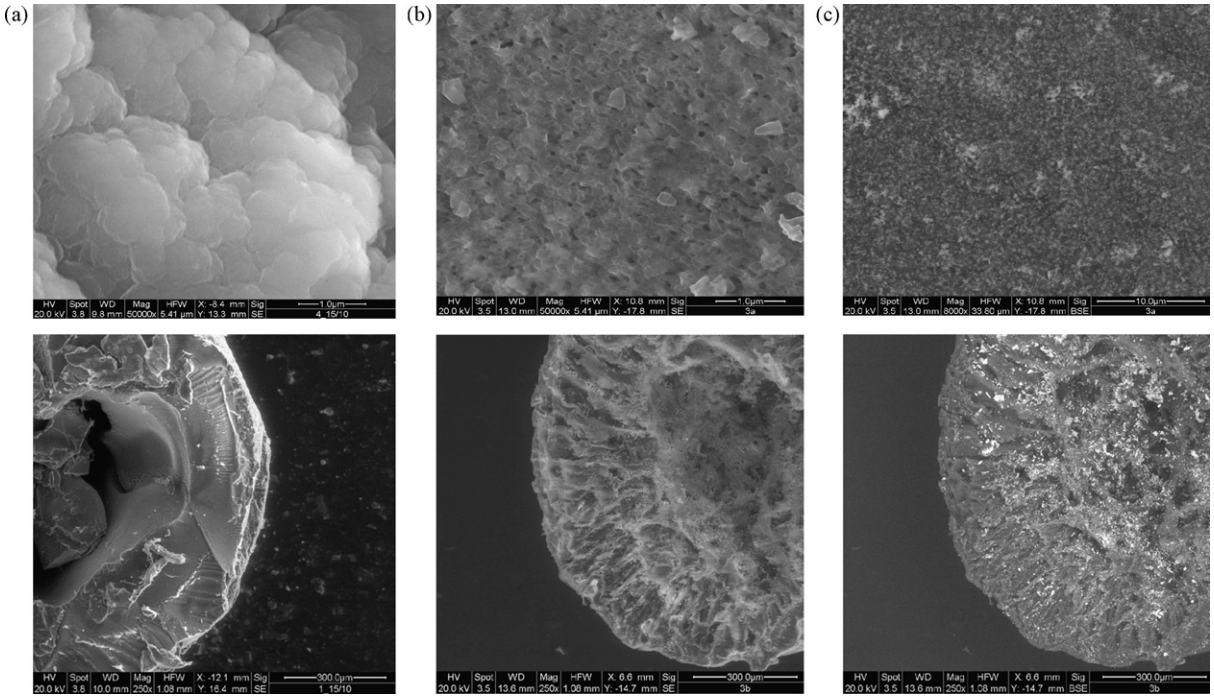


Fig. 2. Top, SEM of shell surface (magnification) of (a) PVDF microcapsules and (b) PVDF catalytic microcapsules, respectively and (c) BSE analysis of PVDF catalytic microcapsules; (bottom) SEM of cross-section of microcapsules.

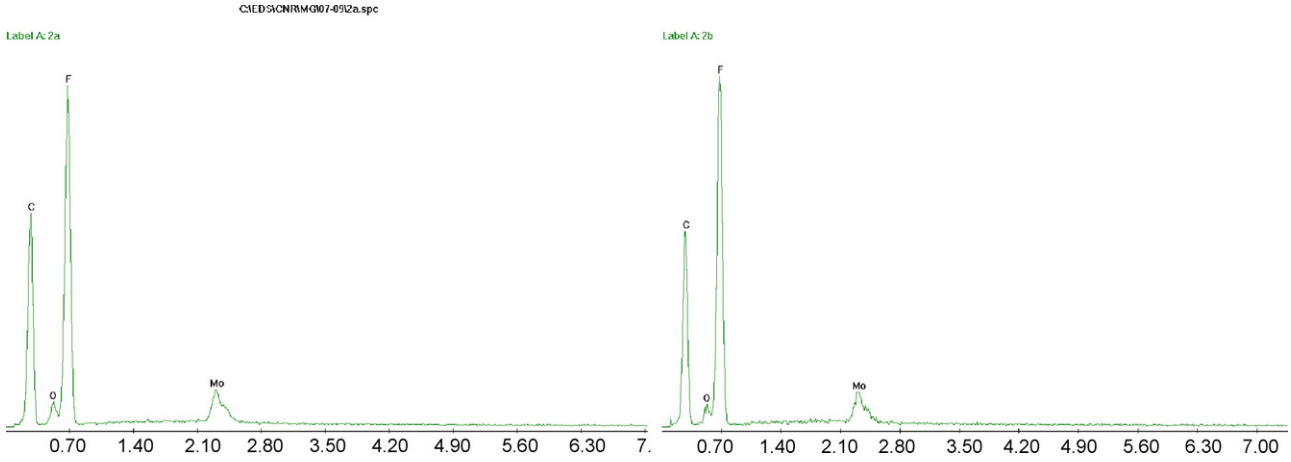


Fig. 3. EDX analysis of two slices 30 μm × 30 μm of PVDF catalytic microcapsules shell surface.

addition of inorganic salts in casting dope of PVDF/DMF, during the course of membrane formation, was reported for flat membranes and hollow fibers by several authors [37–40]: the presence of salts in the casting solution enhances the liquid-liquid demixing giving to more porous structures. In this work, the entrapment of ammonium molybdate inside the PVDF polymeric matrix and the absence of loss of the catalyst during the microcapsule preparation has been guaranteed by the use of a soft coagulation bath, a mixture 1:1 of water and isopropanol, rather than a hard non-solvent as pure water. The demixing rate obtained varying coagulant hardness can tune the affinity of ammonium molybdate to DMF/water system or PVDF, inducing in the first case a ''salt out'' and in the second case a ''salt in'' phenomenon, respectively [37].

In Fig. 5, thermograms of PVDF catalytic microcapsules, PVDF microcapsules and ammonium molybdate are shown. The temperature of melting (T_m) of PVDF catalytic microcapsules was 172.8°, that of PVDF microcapsules without catalyst, slightly higher, 174.4°. Different thermal behaviour for the two samples was observed analyzing the cooling curves. In fact, PVDF catalytic microcapsules were characterized by two temperature of crystallization, T_c: at 213 °C due to ammonium molybdate crystallization in the polymeric matrix; at 140 °C, T_c of PVDF in its β form. However, PVDF microcapsules showed peak of crystallization (T_c = 140 °C) with an evident shoulder at higher temperature (144–146 °C).

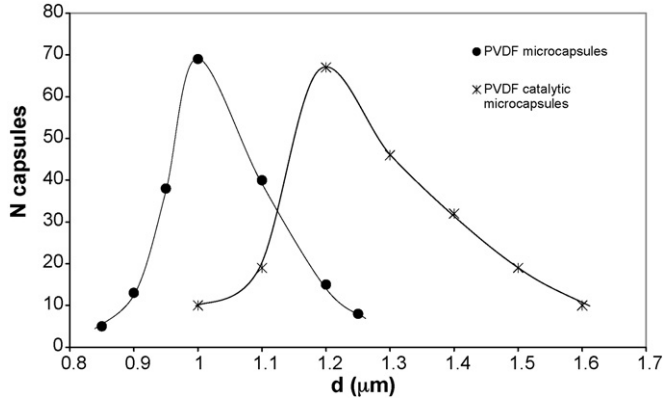


Fig. 4. Pore size distribution of the PVDF microcapsule membranes (a) with (20 wt%) and without $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$.

This was due to the transformation from α to β phase crystals of PVDF as being consistent with the XRD results (see below). Data from the literature [41] support the idea that the double crystallization peaks observed in the DSC experiment on PVDF are due to a polymorphic structure peculiar to this polymer. This is in accord with that observed by Lin et al. [37] for flat membranes from the system PVDF/DMF/$LiClO_4$: they observed also on the basis of DSC analyses that increasing the content of additive salt, i.e. the viscosity of the system, PVDF crystallites in β form predominate, whilst a mixture of α and β types crystallites was observed in absence of salt in casting solution. The influence of the ammonium molybdate on the crystallite forms present in the microcapsules has been examined by means of X-ray analysis.

In Fig. 6a, peak at $2\theta = 9.6°$ indicated the presence of ammonium molybdate in the polymeric matrix whilst an intense peak at $2\theta = 20.7°$ corresponded to the superimposed peaks β(1, 1, 0) and β(2, 0, 0) of the PVDF β-form crystals. Neat PVDF microcapsules exhibited a mixture of β-form and α-form crystals, where planes α(1, 0, 0) and α(0, 2, 0) give rise to a single peak at $2\theta < 20°$, i.e. a shoulder at $2\theta = 19.7°$ on the peak at $2\theta = 20.2°$ (Fig. 6b).

Therefore, the addition of ammonium molybdate into the PVDF microcapsules leads to complete crystal transformation from α- to β-form crystals.

The presence and influence of ammonium molybdate on crystal form of PVDF microcapsules has been confirmed by means of FT-IR analysis (Fig. 7).

The signals at 945, 1431–1404 and 3402 cm^{-1} are characteristics for ammonium molybdate, due to Mo=O stretching, NH_4^+ bending and stretching vibrations, respectively.

The intense peak at 839 cm^{-1} represents the CH_2 rocking and CF_2 asymmetric stretching in the β-phase crystals of PVDF, and also a known out-of phase combination [42].

In Fig. 8, swelling results of PVDF catalytic microcapsules in pure BzOH and acetonitrile, and mixtures of the two

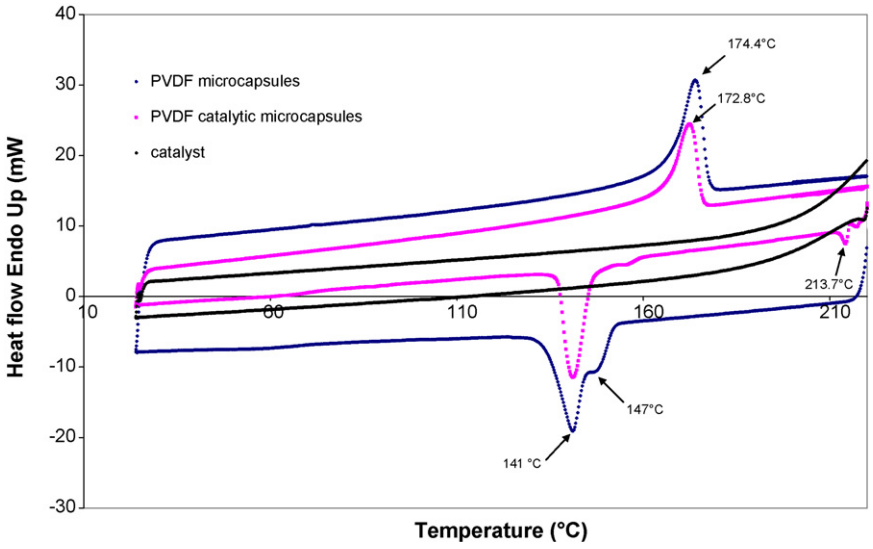


Fig. 5. DSC thermograms of neat, catalytic PVDF microcapsules and catalyst, $(NH_4)_6Mo_7O_{24}$: first cooling and second heating curves.

components have been reported. The lowest swelling value was obtained using pure BzOH whilst the highest value was observed with pure acetonitrile. In other words, the swelling of the PVDF catalytic capsules increased with the quantity of acetonitrile. It must be emphasized that during all of swelling experiments nor leaching of the ammonium molybdate was observed. This is due to two facts: ammonium molybdate is not soluble neither in BzOH and acetonitrile; the interactions between the catalyst and the polymer PVDF are enough to avoid leaching.

Additional proof of successful entrapment of catalyst inside polymeric matrix was given by the different colorimetric reactions between the catalytic PVDF microcapsules and the reaction reagents, i.e. the substrate (BzOH) and the oxidant

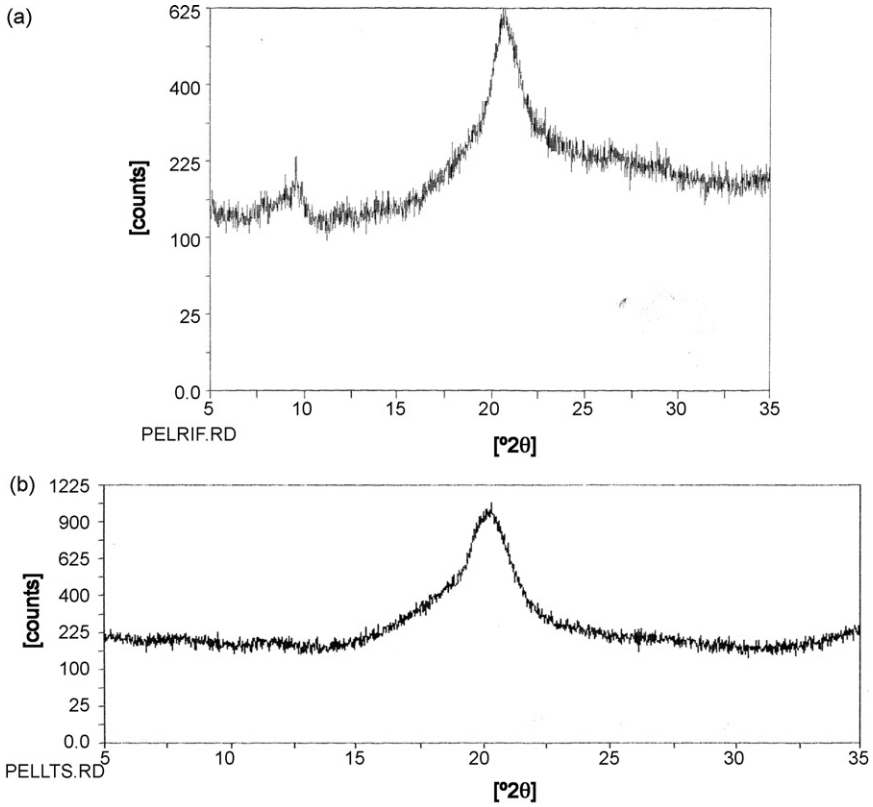


Fig. 6. XRD of catalytic (a) and neat (b) PVDF microcapsules.

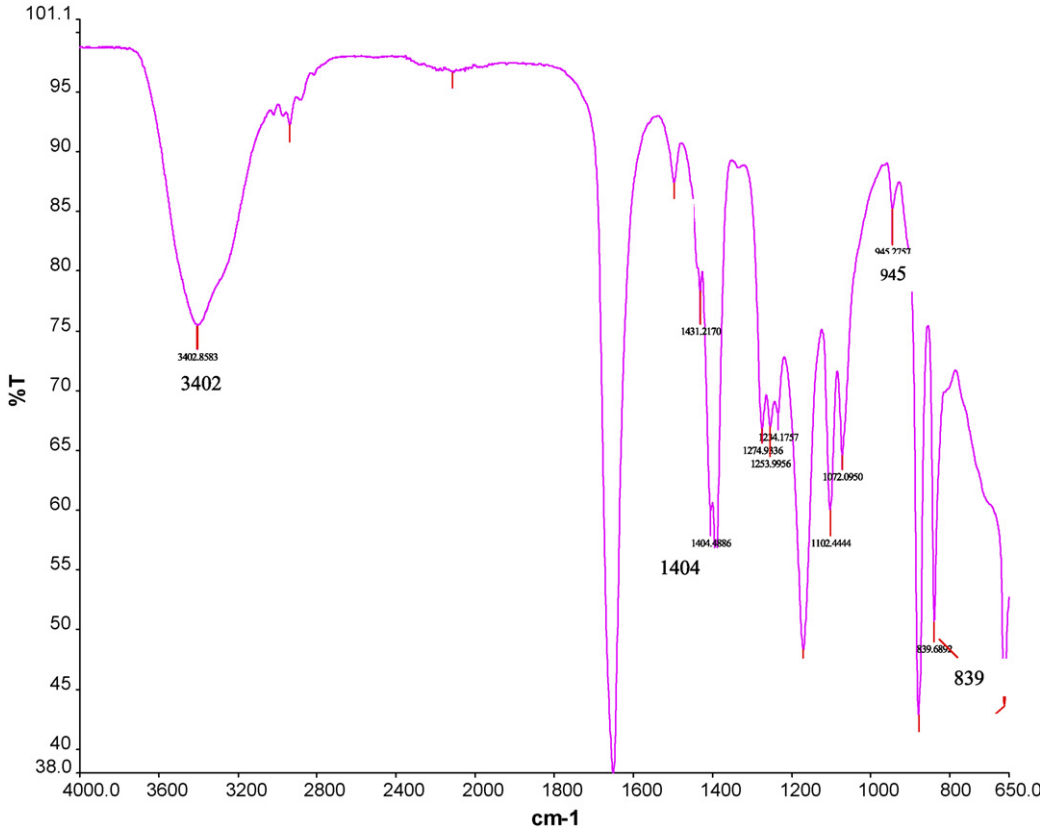


Fig. 7. FT-IR spectra for PVDF catalytic microcapsules.

(hydrogen peroxide). In fact, in contact with BzOH, the PVDF catalytic microcapsules from the original white (Fig. 9a) turn to intense bleu colour (Fig. 9b); in hydrogen peroxide solution, the colour variation was to green-yellow (Fig. 9c). No analogue colorimetric reactions occurred with PVDF microcapsules without catalyst inside.

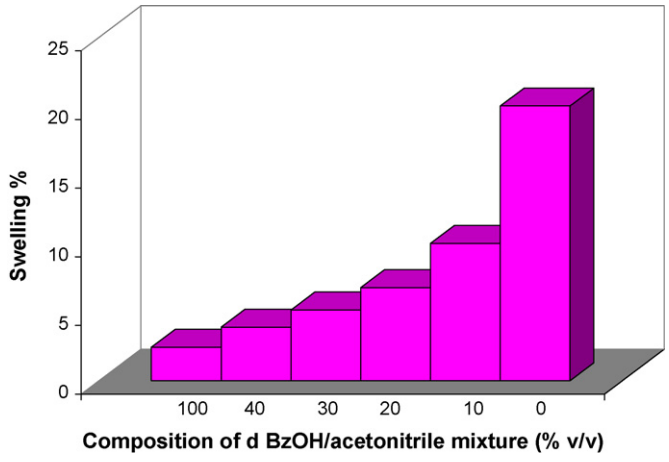


Fig. 8. Swelling data (at 25 °C) of PVDF catalytic microcapsules in mixtures of BzOH/acetonitrile at different compositions.

3.2. Microcapsule activity

The BzOH oxidation to BzH happens by the following reaction:

$$C_6H_5CH_2OH + H_2O_2 \xrightarrow{cat} C_6H_5CHO + 2H_2O$$

Firstly, the reaction was carried out in solvent free conditions and the effect of reaction temperature, ratio substrate/hydrogen peroxide was investigated. Then, the reaction was carried out using a mixture BzOH/acetonitrile 10% (v/v), to study the influence of polymer swelling on substrate conversion.

Effect of reaction temperature on the progress of oxidation of BzOH was studied in the temperature range 323–363 K. The experimental results are reported in Figs. 10 and 11. It is observed in these experiments that BzOH conversion to BzH increased as temperature was raised, without a substantial loss of reaction selectivity (>99%).

In fact, conversion of BzOH to BzH from 6% at 323 K increased up to 56.0% operating at 363 K. The same trend was observed for hydrogen peroxide conversion: from 5.9 to 56.3%. The noticeable effect of reaction temperature on the production of BzH was clearly visible from the start of the reaction (Fig. 11). The production of BzH proceeded for 120 min with a similar trend operating at 323 and 343 K (20 and 30 g/l of BzH, respectively) whilst at 363 K an higher concentration of product

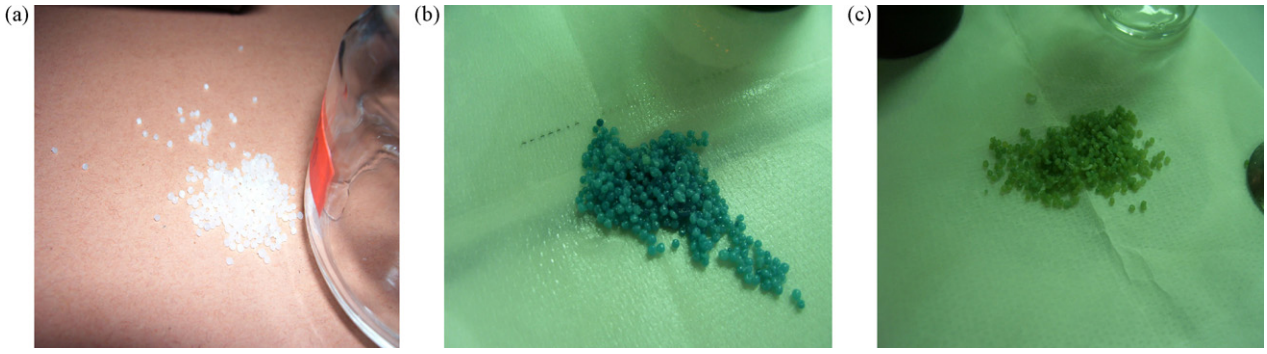


Fig. 9. Pictures of PVDF catalytic microcapsules (a) dry and after immersion in pure BzOH (b) and (c) in aqueous solution 30% (v/v) of H_2O_2.

was achieved (94 g/l). A more pronounced difference in the production of BzH at 323 and 343 K became evident from 130 to 240 min.

Chaudhari and Sawant [43] observed the same strong influence of the temperature on the progress of the BzOH oxidation made in a conventional reactor with the catalyst in the H_2O_2 aqueous phase. They classified this reaction as very slow reaction, kinetically controlled for which reaction temperature influences the progress of the reaction significantly.

In this work, temperature effected also the diffusion of the reagents across the polymeric catalytic microcapsules: increasing the reaction temperature, the diffusion to the catalytic sites on and inside catalytic microcapsules was enhanced.

Regarding the amount of hydrogen peroxide added in the aqueous phase, the results, reported in Figs. 12 and 13, evidenced that increasing the ratio oxidant: BzOH from 1:1 to 2:1, the conversion to BzH did not increase, but it was lower. In this work, we used catalytic polymeric microcapsules based on slightly hydrophobic material, PVDF, that acts at the interface between the two immiscible phases, organic and aqueous. When H_2O_2:BzOH was 2:1, abundance of H_2O_2 is present in the aqueous phase but the quantity that effectively reacts is controlled by the diffusion in the boundary layer at the interface PVDF microcapsule-aqueous phase. Globally the difference between the two cases depends on the H_2O_2 decomposed: when the oxidant is added in equimolar quantity with respect to the substrate, it is preserved by decomposition. Operating with a ratio BzOH:H_2O_2 of 1:2, the excess of oxidant did not react but it was decomposed.

To evaluate the effect of solvent swelling on the reactivity, the reaction was carried out at 323 K using a mixture of BzOH/acetonitrile 10% (v/v) containing the same amount of BzOH used to study the reaction in neat conditions. Interestingly, the results, reported in Fig. 14, show that using acetonitrile as reaction solvent and therefore working in dilute conditions, the conversion to product is higher than that obtained in neat conditions (21.5 and 6%, respectively). However, the selectivity to BzH using acetonitrile as solvent is lower (97.3%) than that observed (99.3%) operating in neat conditions. These results can be explained on the basis of mechanism reaction involved using PVDF catalytic microcapsules.

As reported by different authors, for derivatives of Mo, V and W, the metal precursor adds hydrogen peroxide in an equilibrium process largely shifted to the right [44]. The intermediate **1** is thus formed in which *n* is usually 1 or 2 (Scheme 2).

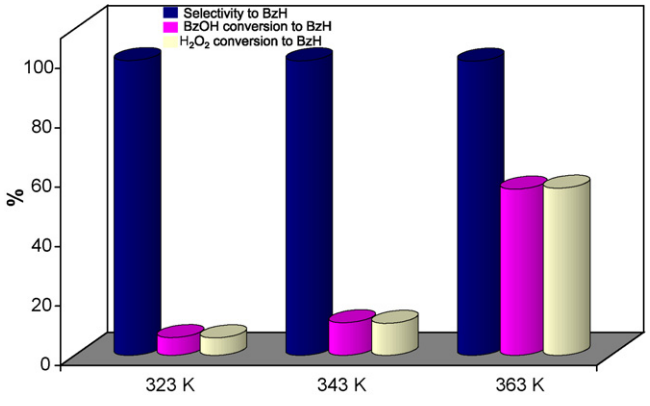


Fig. 10. Selectivity[a], BzOH[b] and H_2O_2[c] conversion to BzH at different reaction temperatures (reaction time 4 h). [a]Selectivity to BzH = [mmol BzH/(mmol BzH + mmol BzA)] × 100. [b]BzOH conversion to BzH = (mmol BzH/mmol BzOH initial) × 100. [c]H_2O_2 conversion to BzH = (mmol BzH/mmol H_2O_2 initial) × 100.

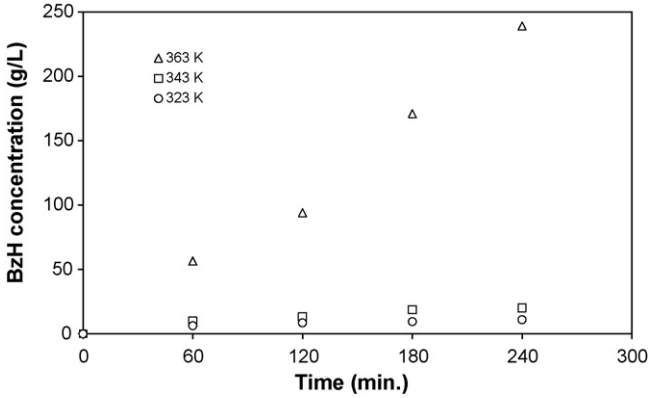


Fig. 11. BzH concentration in the organic phase *vs.* time at different reaction temperatures.

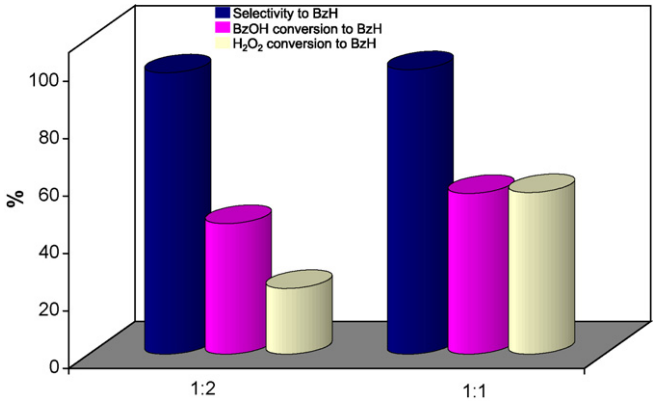


Fig. 12. Selectivity, BzOH and H_2O_2 conversion at different substrate/oxidant ratio (reaction time = 4 h; T = 363 K).

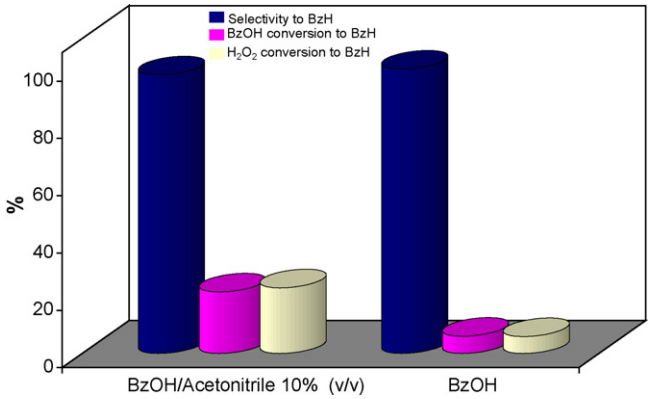


Fig. 14. Selectivity, BzOH and H_2O_2 conversion to compare the use of 10% (v/v) BzOH in acetonitrile with that of pure BzOH (reaction time = 4 h; T = 323 K).

The peroxometal complex **1** is the real oxidant.

Using the catalytic microcapsules, the reaction proceed with the following steps: (i) formation of intermediate **1** on the microcapsule catalytic porous shell; (ii) interfacial oxidation reaction of BzOH; (iii) BzH (insoluble in the aqueous phase) extraction in the organic phase (BzOH), using neat conditions (Scheme 3). The occurrence of step 1 was easily observed on the basis of colour change of the catalytic microcapsule shell from bleu (in presence of pure BzOH) to green-yellow when H_2O_2 is added in the reactor (see Fig. 9).

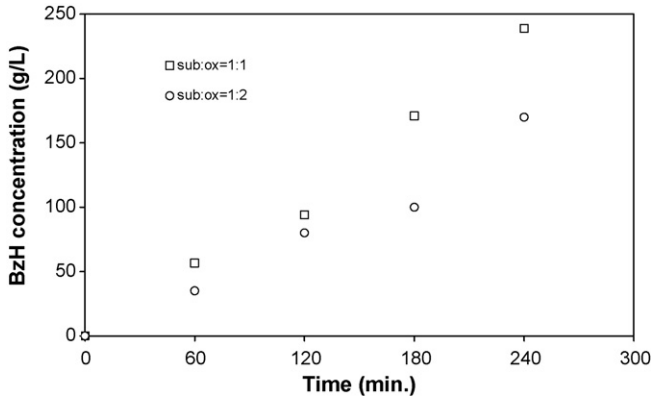
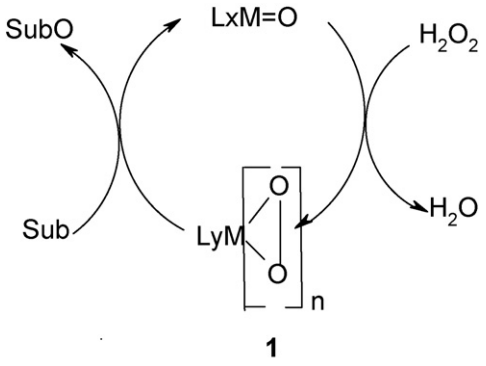
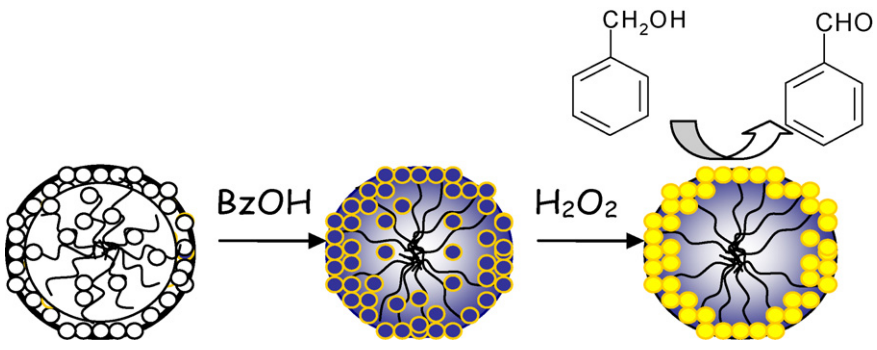


Fig. 13. BzH concentration in the organic phase varying the substrate/oxidant ratio (T = 363 K).

As above reported (Fig. 8), the swelling of the catalytic microcapsules increased with the percentage of acetonitrile to BzOH, due to the more intense interactions between the polar solvent and PVDF polymeric chains compared to those with the lipophilic BzOH. This phenomenon increased the availability of Mo catalyst entrapped in the polymeric microcapsules, i.e. the active sites number. In other words, using the mixture BzOH/acetonitrile 10% (v/v) both the reaction steps (i and ii) were favoured. The lower selectivity observed is due to the fact that the system, in this case, is monophasic (acetonitrile was solvent for organic and aqueous phases) and the product BzH is not extracted to the organic phase where it takes shelter from



Scheme 2. Mechanism of peroxometal catalysis.



Scheme 3. Reaction mechanism for the PVDF catalytic microcapsules.

over-oxidation, as it occurs operating in neat conditions, i.e. using biphasic system.

The regeneration of the heterogeneous systems is another important subject for practical applications. The PVDF catalytic microcapsules can be used in further catalytic runs without a loss of activity. No catalytic properties were observed using the PVDF microcapsules without the catalyst entrapped for the BzOH oxidation.

4. Conclusion

In this work, it was possible to demonstrate, for the first time, that using PVDF catalytic microcapsules as heterogeneous catalyst and interphase contactor in a biphasic reaction in neat conditions is feasible.

BzOH can be oxided selectively to BzH with hydrogen peroxide as oxiding agent and ammomium molybdate as catalyst entrapped in the polymeric microcapsules.

With the new PVDF catalytic microcapsules, the reported results show that using pure BzOH without solvent reaction, hydrogen peroxide in equimolar ratio with BzOH, a reaction temperature of 363 K the best system performance in terms of selectivity to BzH (99.1%) and BzOH conversion (56%) have been obtained. Compared with conventional reactors, the catalytic microcapsules play a role similar to a phase transfer catalyst without need of organic solvents.

The catalytic microcapsules prepared are stable and recyclable without loss of activity in successive catalytic runs; furthermore, no catalytic activity was detected for the microcapsules prepared without the catalyst.

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